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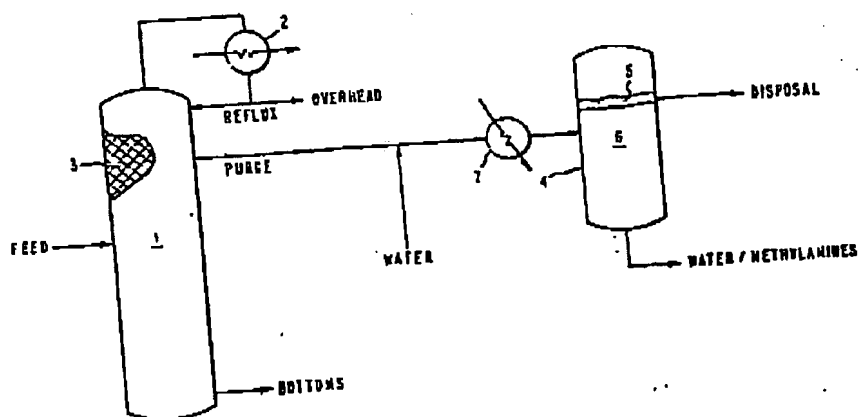
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(54) Methylamines purification process and products thereof.

(57) The distillative refining of methylamines containing higher amine impurities which accumulate in the distillation column (1), tending to cause flooding and product contamination, is improved by purging the column at the point (3) the impurities concentrate, mixing the purge with water to form two phases (5,6), separating the phases and recycling the water phase for recovery of its methylamine content.

EP 0 037 695 A1

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-1-

METHYLAMINES PURIFICATION PROCESS  
AND PRODUCTS THEREOF

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The invention relates to the purification of methylamines.

Methylamines are conventionally produced by the silica-alumina catalyzed reaction of methanol and ammonia at temperatures of 350-450°C and pressures of 200-350 psig. The reaction produces an equilibrium distribution of ammonia, trimethylamine, monomethylamine, dimethylamine, water, methanol and higher amine impurities. The methylamines are separated by distillation; and the unreacted ammonia, methanol and some methylamines are recycled to the reactor. Byproduct water is usually purged from the system.

The distillation of the crude product can be quite complex, depending upon the product mix desired. In most operations, the ammonia is first separated off by distillation under pressure. Thereafter, the methylamines are separated, both from each other and from the water and methanol, in additional distillation columns.

During the distillation of the methylamines, the higher amine impurities tend to become trapped in the refining train, usually in a column that takes a methylamine overhead and has a water-rich phase at the base. In such a column, the higher amines accumulate in certain regions of the column and when their concentration becomes high

enough to restrict vapor-liquid traffic, the column floods, resulting in contamination of the distilled product.

The process for distillation of methylamines containing higher amine impurities can be improved by:

- (i) feeding crude methylamines into a distillation column;
- (ii) taking off a methylamines fraction as overhead and a water-rich phase as bottoms;
- (iii) purging the distillation column at an area where the impurities concentrate at a rate sufficient to maintain the impurities level below the flooding or upset concentration;
- (iv) mixing the purge with water or salt water to promote two phases such that the methylamines content of the resulting water layer does not exceed 25% by weight;
- (v) separating the water layer from the water-immiscible higher amines layer; and
- (vi) recycling the water layer to the process for recovery of its methylamines content.

By "methylamines" is meant any of mono-methylamine (MMA), dimethylamine (DMA) or trimethylamine (TMA) or their mixtures.

The process of the invention results in substantial reduction or even elimination of process upset and product contamination caused by column flooding with purge flows less than about 2% of the total feed to the column. In operating the process, the yield loss can be held to less than 0.1% therefore providing a corresponding reduction in environmental disposal problems.

The purge is removed from the column at a rate sufficient to maintain the impurities level in the column below the flooding concentration. This rate can be determined by experience or analysis of the purge. In most embodiments, the total purge can range from 0.1-5%

0037695

-3-

of the feed to the column. It is desirable to have the purge rate as small as possible, and rates of less than 2% of the feed flow are preferred.

Water is mixed with the purge to promote two liquid phases, a light phase containing the impurities and a heavier water phase that contains the methylamines. The amount of water added to the purge should be controlled so that the methylamine content of the water does not exceed 25% by weight. The process can be operated at concentrations as low as 1% by weight, but the preferred concentration range will be between 10-20% by weight, with most preferred concentration being about 15% by weight. The light phase will normally contain about 80% by weight impurities.

In many cases, the solubility of organic impurities in the water phase can be decreased if one or more water-soluble inorganic bases and salts/or one or more water-soluble inorganic salts are added to the water. Preferred for use are bases such as the alkali and alkaline earth metal oxides and hydroxides (e.g.,  $\text{Na}_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{BaO}$  and  $\text{Ba}(\text{OH})_2$ ), neutral salts (e.g.,  $\text{NaCl}$ ,  $\text{KCl}$  and  $\text{Na}_2\text{SO}_4$ ); and basic salts (e.g.,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_2\text{B}_4\text{O}_7$ ). The amount of salt or base added is not critical, and the maximum amount added is that necessary to form a three-phase system, i.e., three liquid or two liquid and one solid base.

In step (v), the water purge mixture is cooled to a temperature below the boiling point of any of the impurities and aqueous methylamines present. When operating at atmospheric pressure, the temperature after cooling is about 20-40°C. This cooling is desired to avoid flashing of the methylamines from the water phase during separation and to reduce the solubility of the impurities in the water phase. The higher the temperature, the more likely the methylamines will flash; and the higher the methylamine concentration in the water phase, again it is more likely that flashing will occur. At atmospheric

-4-

pressure, the preferred temperature is about 30°C and the preferred concentration of methylamine is about 15% by weight. The cooled water-purge mixture is then separated into its two component phases.

The following is a description, by way of example only, of one embodiment of the invention, reference being made to the accompanying schematic drawing which is a flow diagram of the process.

Crude methylamine is manufactured in a reactor by a conventional method and a resulting crude methylamine stream is fed to the distillation column 1 shown in the drawing. In the production of the crude methylamine trace impurities are also manufactured. These impurities are predominantly higher amines and include higher alkylamines and diamines, alkyl-substituted pyridines and pyrroles, and aliphatic amides. As indicated earlier, the impurities have physical properties that cause them to trap or accumulate in various columns in a refining train. This accumulation can occur in several regions of a column that has a methylamines overhead and a water-rich phase at the base.

When the impurities accumulate to a sufficient extent to restrict vapor-liquid traffic within the column, the column will flood. This flooding causes a process upset and product contamination.

The distillation column 1 contains the appropriate number of trays. In this column, the crude methylamine stream is distilled under pressure, e.g., 150 psig, to produce a water-rich bottoms phase and a methylamine overhead. The overhead is condensed in condenser 2 and part fed back into the column 1 as reflux, the remainder being taken off as raffinate for further refining or storage or recycle to synthesis.

In region 3 in the column, the concentration of the higher amine impurities is at or near its maximum. The locality of this region can be determined by tray-to-tray analysis of the column composition, and a purge will

-5-

0037695

preferably be taken from the region of the column having the highest impurity concentration. In some embodiments, there will be several regions in the column where the impurities concentrate; in such cases, the purge can be taken from more than one region.

The purge will be removed from the column at a rate sufficient to maintain the impurities level in the column below the flooding concentration. This rate can be determined by experience or analysis of the purge. As mentioned earlier, it is desirable to have the purge rate as small as possible, and rates of less than 2% of the feed flow are preferred.

Water is then mixed with the purge to promote two liquid phases, a light phase containing the impurities and a heavier water phase that contains the methylamines. The amount of water added to the purge should be controlled so that the methylamine content of the water is at the most preferred 15% by weight level mentioned earlier. The light phase will contain around 80% by weight impurities.

Salt or base is added to the water, as mentioned earlier, to ensure formation of a three-phase system. The water-purge mixture is then cooled to a temperature below the boiling point of any of the impurities and aqueous methylamines present in a cooler 7; at atmospheric pressure this is about 20-40°C.

The cooled water-purge mixture is fed into a decanter 4 or other liquid-liquid phase separator where the two phases are formed. The light phase 5 containing about 80% impurities, i.e., the higher boiling amines, is then removed from the decanter for disposal or other use. The water phase 6 containing the methylamines is then recycled to the distillation train for recovery of the methylamines.

The process permits the continuous removal

of impurities to maintain column stability and product quality with a minimum yield loss. The addition of water or water with base or salt promotes the formation of the two phases, and 50-80% of the impurities present are removed.

#### EXAMPLES

The following Examples are intended further to illustrate the invention:-

##### Example 1

One hundred parts of purge (43% water, 49.4% methylamines, 7.6% impurities) are mixed with 265 parts of water and cooled to 25°C. The resulting two-phase system is decanted. The upper-liquid phase, 5.2 parts analyzed: 0.7% H<sub>2</sub>O, 10.6% methylamines and 88.7% impurities. The lower liquid phase, 359.8 parts, analyzed: 85.6% H<sub>2</sub>O, 13.6% methylamines and 0.8% impurities.

##### Example 2

One hundred parts of purge (49.9% H<sub>2</sub>O, 45.7% methylamines, 4.4% impurities) are mixed with 300 parts of 5% NaOH in water and cooled to 25°C. The resulting two-phase system is decanted. The upper liquid phase, 2.6 parts, analyzed: 0.9% H<sub>2</sub>O, 8.4% methylamines and 90.7% impurities. The lower liquid phase, 397.4 parts, analyzed: 3.8% NaOH, 84.3% H<sub>2</sub>O, 11.4% methylamines and 0.5% impurities.



CLAIMS:

1. A process of distilling crude methylamines which process comprises (i) feeding crude methylamines into a distillation column; (ii) taking off a methylamines fraction as overhead and a water-rich phase as bottoms; (iii) taking a purge from a region in the column where the impurities concentrate, the purge rate being sufficient to avoid a flooding concentration of impurities in the column; (iv) adding water to the impurities-containing purge to form a water-immiscible phase containing impurities and a water phase containing methylamines, the amount of water added being sufficient to keep the methylamine content of the water phase below 25% by weight; (v) cooling the water-immiscible phase and the water phase to a temperature below the boiling point of the impurities and aqueous methylamines; (vi) separating the two phases; and (vii) recycling the water phase for recovery of its methylamine content.
2. A process as claimed in Claim 1 wherein the water of the water phase formed in step (iv) contains a water-soluble inorganic base or salt.
3. A process as claimed in Claim 2 wherein the base or salt is  $\text{Na}_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{BaO}$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_3\text{PO}_4$  or  $\text{Na}_2\text{B}_4\text{O}_7$ .
4. A process as claimed in any one of Claims 1 to 3 wherein the amount of water added in step (iv) maintains the methylamine content of the water phase below 15% by weight.
5. A process as claimed in any preceding claim wherein the cooling in step (v) is effected at atmospheric pressure to reduce the temperature of the phases to a value from  $20^\circ\text{C}$ . to  $40^\circ\text{C}$ .
6. A process as claimed in any preceding claim wherein the separation of the two phases in step (vi)

is conducted using a decanter.

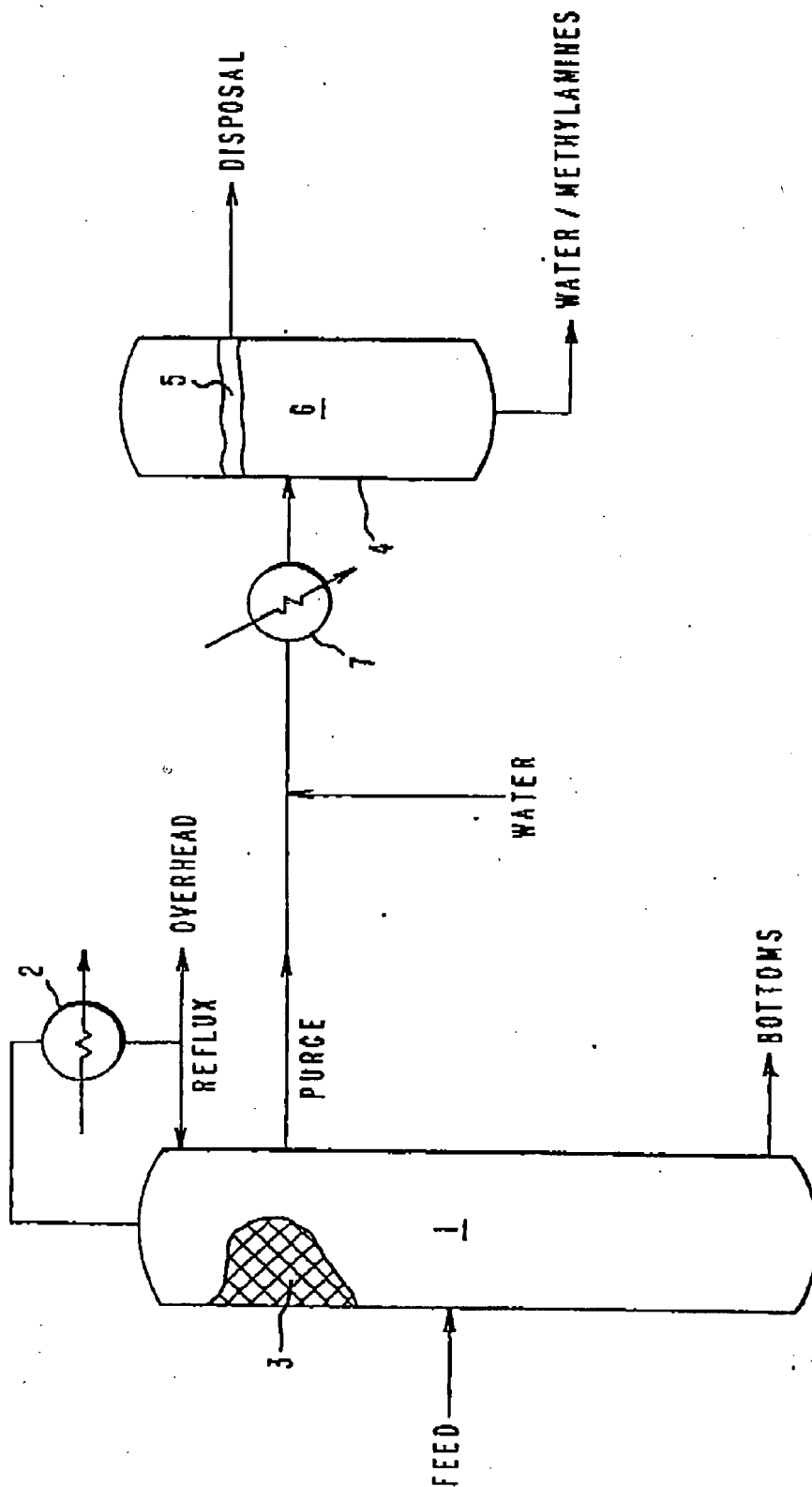
7. A process as claimed in Claim 1 and conducted in apparatus substantially as hereinbefore described with reference to, and as illustrated schematically in, the accompanying drawing.

8. A process for distilling crude methylamines and including treatment of a purge substantially as hereinbefore described in either of Examples 1 and 2.

9. Monomethylamine, dimethylamine, trimethylamine, or a mixture of two or more thereof, obtained by a process as claimed in any preceding claim.

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1 / 1



0037695

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## EUROPEAN SEARCH REPORT

Application number  
EP 81301358.8

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	DD - A - 118 414 (DEHMELT et al.) + Claims 1-3 + -----	1,9	C 07 C 87/08 C 07 C 85/26
			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			C 07 C 85/00 C 07 C 87/00
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background C: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
X	The present search report has been drawn up for all claims		
Place of search VIENNA		Date of completion of the search 16-06-1981	Examiner REIF

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